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# EFFECT OF NONCONDUCTING INCLUSIONS ON THE ELECTRICAL CONDUCTIVITY OF AN ELECTROLYTE

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In industrial electrolysis the electrolyte often contains nonconducting inclusions - solid suspended material or, still more frequently, bubbles of gas. Such inclusions lower the conductivity of the electrolyte. Even the presence of conducting inclusions, ~~as for instance~~ particles of carbon in a molten electrolyte, lowers conductivity, because polarization phenomena make impossible the passage of current through these inclusions.

The degree of the lowering of conductivity does not depend on the degree of filling only, but also on the shape and position of the inclusions. If the inclusions have the shape of cylinders the axes of which are lie in the direction of the current, the reduction of the conducting cross-section will be equal to the relative filling of the volume. The relative conductivity of such a system will be

$$K_c = \text{[illegible]} \qquad (1)$$

where [illegible] is the relative conductivity of the pure electrolyte, the relative conductivity of the electrolyte containing the inclusions, and p the relative filling [packing], which is equal to the volume of inclusions per unit of the total volume.

Already in 1892 Rayleigh [1] derived mathematical expressions for the electrical conductivity of heterogenous systems containing either inclusions having the shape of cylinders with axes disposed perpendicularly to the direction of the field or spherically shaped inclusions.

Later Runge [2] repeated the same calculations and after introducing some corrections arrived at the expression

$$K_c = 1 - \frac{2p}{\frac{1+\chi_1}{1-\chi_1} + p - 0.30584\frac{1-\chi_1}{1+\chi_1}p^4 - 0.013363\frac{1-\chi_1}{1+\chi_2}p^8 \ldots} \qquad (2)$$

for cylindrical inclusions, and the expression

$$K_c = 1 - \frac{3p}{\frac{2+\chi_1}{1-\chi_1} + p - 0.523\frac{1-\chi_1}{4/3+\chi_1}p^{10/3} + \ldots} \qquad (3)$$

for spherical inclusions, where $\varkappa_1$ is the specific conductivity of the inclusions (specific conductivity of the medium $\varkappa_2$ = 1), while $K_c$ and p have the same meaning as in (1).

In the case of ~~For~~ nonconducting inclusions ( $\varkappa_1$ = 0), equations (2) and (3) become

$$K_c = [illegible] \qquad (2a)$$

$$K_c = [illegible] \qquad (3a)$$

while with low relative degrees of filling (when p ≪ 1 and the higher powers of p are neglected) we have

$$K_c = [illegible] \qquad (2b)$$

$$K_c = [illegible] \qquad (3b)$$

Maxwell [3] derived another expression for a heterogeneous system with spherical inclusions. In the case of nonconducting inclusions, Maxwell's equation becomes identical with (3b).

The formula for the case of filling with cylinders having axes that are perpendicular to the direction of the current has been checked by us with the aid of a graphical construction of the field (as well as ~~and~~ experimentally.

Let us assume that the cylinders are arranged hexagonally, as shown in Figure 1. We shall ~~describe~~ indicate the distance between the cylinders by saying that d = mr, where r is the radius of the cylinders and m the factor. The elementary cells of the field are rectangles I, II, and III (cf Figure 1), which differ only in orientation. The sides of the cell are a = 0.5 d = 0.5 mr and b = a $\sqrt{3}$ = 0.866 mr . The relative filling of the volume is

$$p = \frac{0.5\pi r^2}{ab} = \frac{3.63}{m^2} \qquad (4)$$

If the cylinders touch each other ($n = 2$), the conductivity of the system is $K_c = 0$, while according to (4), $p = 0.909$.

The graphical construction of the field is simplest when the direction of the field is along the side a or side b of the elementary cell. An example of the construction of the field by the method of curvelinear squares ~~is~~ when $d=2.2\,r$ is shown in Figure 2. The number of force tubes z may be set arbitrarily, depending on practical convenience (in Fig. 2, $z=4$).

Let us designate the conductivity of the elementary section in the absence of inclusions and in the case of a uniform field with $K_o'$ and the corresponding conductivity in the presence of inclusions with $K_c'$, and then calculate the relative area ~~conductivity~~

$$K_c = \frac{K_c'}{K_o'}$$

Then, in the absence ~~presence~~ of inclusions, we have

$$K_o' = \frac{a}{b}\chi = \frac{\chi}{\sqrt{3}} \qquad (5)$$

(because according to Fig. 1, $b = a\sqrt{3}$) where $\chi$ is the specific conductivity of the electrolyte; and in the presence of inclusions

$$K_c' = \frac{z}{w_c}\frac{i}{u} \qquad (6)$$

where i is the strength of the current passing through one tube, u the drop of potential between two ~~equipo~~ isopotential lines, and $w_c$ the number of isopotential lines along the length of the elementary cell determined by counting them ~~a simple count~~ in Figure 2. In equation (6),

$$\frac{i}{u} = \chi\frac{\Delta s}{\Delta l} \qquad (7)$$

where $\Delta s$ is the width of the ~~y~~ force tube and $\Delta l$ the distance between isopotential lines. But according to the conditions of ~~the~~ construction of the field (curvelinear squares), $\Delta s = \Delta l$. Therefore, substituting (7) into (6), we get

$$K_c' = \chi\frac{z}{w_c} \qquad (8)$$


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and finally obtain

$$\varkappa_\varepsilon = \frac{\varkappa_\varepsilon}{\varkappa_0} = \frac{2\sqrt{3}}{W_\varepsilon} \qquad (9)$$

In addition to the field of the cell with d = 2.2 r, we also constructed fields for cells with d = 2.5 r; d = 3 r; and d = 5 r. In the case of d = 3 r, fields were constructed for the flow of current along side b (Figure 3) as well as well as along side a (Figure 4). In view of the fact that O is a ~~symm~~ symmetry point in figures 2, 3, and 4, we have drawn only a part of the elementary cell in figures 3 and 4.

With the direction of the current along the side a, the conductivity in the absence of inclusions will be

$$\varkappa_0 = [illegible] \qquad (5a)$$

and ~~correspondingly~~-- accordingly

$$\varkappa_\varepsilon = \frac{\varkappa_\varepsilon}{\varkappa_0} = W_\varepsilon\sqrt{3} \qquad (9a)$$

Subsequently ~~Further~~ experimental measurements of the lowering of conductivity on filling with nonconducting cylinders were carried out . For this purpose, flat cells 20 cm ~~wide~~ long and 11-12 cm wide were installed. Copper electrodes served as end walls (so that the distance between the electrodes was 20 cm), while the side walls were nonconducting. In the middle part of the cell, a barrier composed of 4 rows of vertical glass cylinders having a diameter of 1.4 cm was mounted. These cylinders were arranged according to the hexagonal system ~~hexagonally~~ (i. e., as shown in Figure 1); the orientation of the barrier corresponded to a direction of the flow of current along side b of the elementary cell I (cf. Fig. 1)

The distances d between the cylinder axes ~~were assumed~~ were adjusted at 2.2 r, 2.5 r, 3 r, and 4 r. The total width of the barrier was accordingly varied between 5.4 and 8.6 cm. The cell was filled up to the height of 1 cm with a solution containing ~~composed~~ 150 g/1 of $CuSO_4.5H_2O$, 20 g/1 of $H_2SO_4$, and 50 g/1 of alcohol. Then , by passing a 50 mA current through the cell and using an electrolytic switch, the potential drop ~~was~~ along the field was measured outside of the barrier and inside it. The measurements showed that a homogeneous field is distorted noticeably only in the immediate vicinity of the barrier, approximately through a distance of one cylinder radius ~~corresponding~~ from the front edge of the ~~cyl~~ first row of cylinders ~~corresponding to one cylinder radius~~.

Knowing the potential gradient $\frac{d u_0}{d x}$ outside of the barrier and the drop of potential inside the barrier per unit of its breadth $\frac{\Delta U_e}{\Delta l_e}$, we find ~~that~~ the relative conductivity in the presence of nonconducting inclusions to be

$$K_e = \frac{\left(\frac{dU_0}{dl_0}\right)}{\left(\frac{\Delta U_e}{\Delta l_e}\right)} \tag{10}$$

In Table 1, ~~t~~the values of $K_e$ determined ~~found~~ graphically are listed side-by-side with those found experimentally. Both series of values agree perfectly. Furthermore, it is of interest that with an equal degree of filling (p = 0.403), but ~~with~~ different orientations of the field perpendicular to each other, the relative conductivity remains the same.

The effect of spherical inclusions was investigated by the experimental method only, because it is difficult to construct and evaluate ~~graphically~~ a three-dimensional field graphically. The cubic-octahedral ~~e~~ arrangement of spheres (Figure 5) was assumed as the basic variation. In this arrangement, the vertical distance between the centers of spheres in two layers amounts to $H = d\sqrt{\frac{2}{3}} = 0.816\ d$. When $H > 2r$ (or $n > 2.45$, because $d=nr$), the layer between the plane passing through the centers of the spheres of one layer and the plane at a distance of 0.5H above it may be regarded as the elementary layer. Such barriers were constructed in a flat cell similar to the one described above by ~~glueing~~ cementing to the ~~bo~~ bottom of the cell four rows of ebonite hemispheres ~~(r~~ (r=0.7 cm) with values of d=4r, 3r, and 2.5r and submergence in electrolyte solution poured in up to a depth of 0.5H.

Barriers with a higher degree of filling were constructed from glass spheres in contact with each other (under application, if necessary, of ebonite halfs and quarters of spheres). Four different arrangements were used:

a) cubic-octahedral arrangment as shown in Fugure 5 for d=2r;

b) cubic-octahedral arrangement as shown in Figure 6 for d=2r (this arrangement is the same ~~as (a)~~ as in case a, but differs from it in orientation: the model has been turned through 120°);

c) hexagonal arrangement as shown in Figure 7;

d) octahedral arrangement as shown in Figure 8.

In variations a and b, the barrier was built up to a height of 3 layers of spheres; in variations c and d, one layer of spheres was used and the electrolyte solution filled in to a depth of H=d=2r. On ~~changing~~ measuring the potential gradient outside and inside of the barrier, the relative conductivity $K_e$ was calculated according to (10). The results are ~~cited~~ listed in Table 2. The first two lines of the table show that with an equal degree of filling the conductivity does not depend on the orientation.

In Figure 9, curve I corresponds to Rayleigh's equation (2a), while curve II


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corresponds to the same curve for spherical inclusions (3a). The values obtained by us for cylindrical inclusions (asterisks ~~indicate these values~~ denote both experimentally found ~~determined~~ and graphically determined values for cylindrical inclusions) as well as spherical inclusions (values shown by circles) up to degrees of filling of the order $p=0.4$ lie near to Rayleigh's first curve (2a). For any arrangement of the spheres, i. e. [cubic-octahedral, hexagonal, ~~and~~ or octahedral [body-centered cube, hexagonal, and face centered cube?], and for all degrees of ~~packing~~ filling up to the densest packing ($p=0.7405$), the experimental values are in good agreement with the empyrical equation

$$K_c = 1 - 1.78p + p^2 \tag{11}$$

In the case of ~~For~~ cylindrical inclusions the experimental values for degrees of ~~packing~~ filling $p$ 0.4 are in sufficient agreement for all technical purposes both with Raleigh's first equation (2a) and our equation (11). At higher degrees of ~~packing by~~ filling cylindrical inclusions produce the peculiar curve IV.

Pfleiderer [4] gives an experimentally determined curve ~~of~~ for the increase of the resistance of an electrolyte as related to the ~~degree of~~ amount of gas which is present, up to a degree of ~~packing~~ filling $p=0.35$. This curve, recalculated for conductivity, is shown in Figure 9 (curve V). For low degrees of filling, this curve is in pretty good agreement with Rayleigh's second equation (3a), but at higher degrees of filling it approaches our equation (11). This gives us reasons to believe that equation (11) may be assumed to have universal validity up to $p=0.4$ with a sufficient degree of precision for all technical purposes. Equation (11) applies for diverse arrangements of the inclusions, including a disordered state. In the case of spherical inclusions of uniform diameter, this equation is valid up to dense packing, i. e. $p=0.7405$.

According to ~~the data obtained by~~ published by Baymakov [5], the presence ~~of 5% or 10%~~ in a cryolite - aluminum oxide melt of 5% or 10% of dispersed carbon raises the specific resistance of the melt by 27 and 40% respectively. Assuming the specific gravity of the carbon to be 1.5 and that of the melt to be 2.05, and changing from resistivity to conductivity, we obtain the two points shown in Figure 9 under letter C. These points agree neither with our data or Pfleiderer's curve, and least of all with ~~Rahel~~ Rayleigh's equation for spherical inclusions.

## Conclusions.

1) The effect of cylindrically and spherically shaped inclusions on the electrical conductivity of an electrolyte was investigated. ~~For~~ In the case of cylindrically shaped inclusions, the investigation was carried out not only by experimental measurements, but also by constructing the field graphically.

2) An empyrical formula for calculating the relative conductance has been advanced. This formula can be used for spherical inclusions with any degree of filling of the volume and for cylindrical inclusions up to degrees of filling not exceeding 0.4 of the total volume

3) ~~A comparison of~~ The results obtained were compared with the theoretically derived formulas of Rayleigh as well as some published experimental data.

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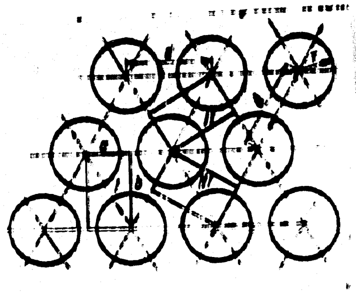


Figure 1. A Field With Cylindrical Inclusions.

I, II, III - elementary cells of the field with axes of cylinders perpendicular to the direction of the field; a and b - sides of the cell; r - radius of inclusions; d - distance between the axes of cylinders.

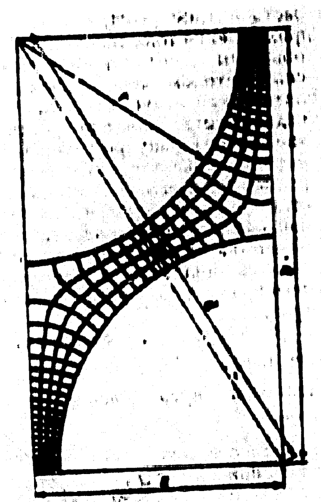

Figure 2. The Field of the Elementary Cell When d = 2.2 r.

The direction of the current is along side b.

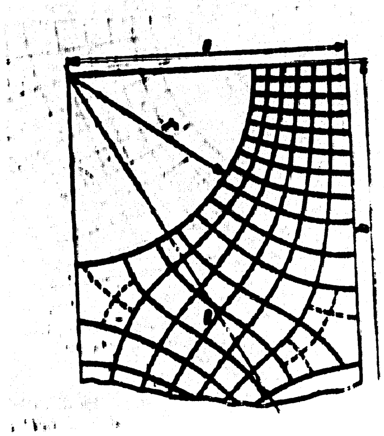

Figure 3. The Field of the Elementary Cell When d = 3r.
The direction of the current is along side b.

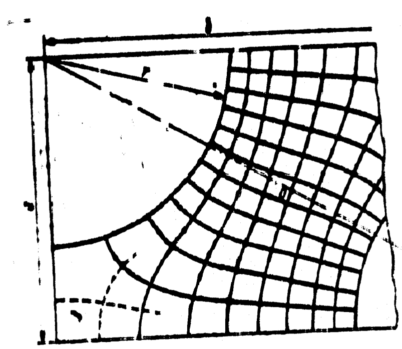

Figure 4. Field of the Elementary Cell When d = 3r.
The direction of the current is along side a.

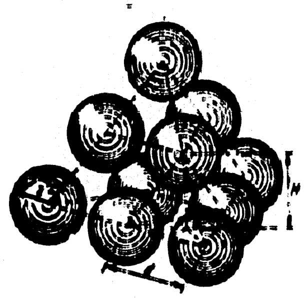

Figure 5. Cubic-Octahedral Arrangement of Spheres.

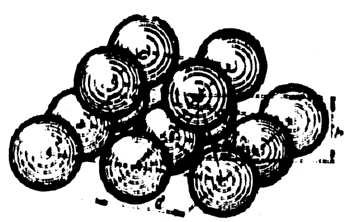

Figure 6. Cubic-Octahedral Arrangement of Spheres With a Different Orientation.

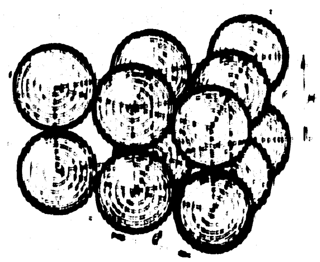

Figure 7. Hexagonal Arrangement of Spheres.

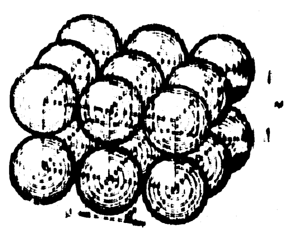

Figure 8. Octahedral Arrangement of Spheres.

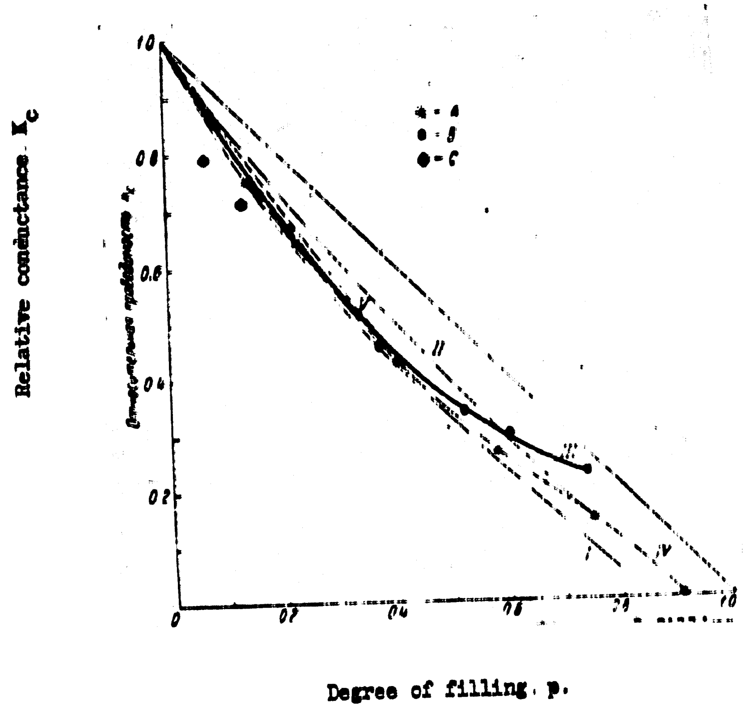


Figure 9. Dependance of Conductance on the Degree of Filling With Nonconducting Inclusions. I - curve corresponding to Rayleigh's equation for cylindrical inclusions (2a); II - to Rayleigh's equation for spherical inclusions (3a); III - to the author's empyrical formula (11); IV - to the author's experimental data for ~~spherical~~ cylindrical inclusions; V - Pfleiderer's experimental curve; A - author's data for cylindrical inclusions, obtained experimentally and by the graphic method; B - author's data for spherical inclusions, obtained experimentally; C - Baymakov's data .

Table 1. Comparison of Values of Relative Conductance Found Graphically and Experimentally in the Case of Cylindrical Inclusions

| No | Distance between axes d | Degree of filling P | Direction of the field | Graphic construction: Number of force tubes z set | Graphic construction: Number of isopotential lines $w_c$ obtained | $K_c$ found graphically | $K_c$ found experimentally | |
|---|---|---|---|---|---|---|---|---|
| | | | | - | - | 0.000 | - | |
| 1 | 2r | 0.908 | Arbitrary | 4 | 49.0 | 0.141 | 0.143 | |
| 2 | 2.2r | 0.750 | Along the side b | 4 | 26.3 | 0.263 | 0.269 | Fig 2 |
| 3 | 2.5r | 0.582 | | 6 | 24.3 | 0.426 | 0.433 | Fig 3 |
| 4 | 3r | 0.403 | | 8 | 11.0 | 0.421 | - | Fig 4 |
| 5 | 3r | 0.403 | Along the side a | - | - | - | 0.640 | |
| 6 | 4r | 0.227 | " " " b | 6 | 13.7 | 0.758 | - | |
| 7 | 5r | 0.145 | " " " b | | | | | |

Table 2. Values of Relative Conductance As Modified By the Degree of Filling and Orientation of [Arrangements of] Spherical Inclusions.

| No | Arrangement of spheres | Distance d between centers of spheres | Degree of filling p | $K_e$ found experimentally |
|---|---|---|---|---|
| 8 | Cubic-octahedral (Fig 5) | 2r | 0.7405 | 0.226 |
| 9 | " " (Fig 6) | 2r | 0.7405 | 0.226 |
| 10 | Hexagonal(Fig 7) | 2r | 0.6046 | 0.297 |
| 11 | Octahedral (Fig 8) | 2r | 0.5236 | 0.338 |
| 12 | Cubic-octahedral (Fig 5) | 2.5r | 0.373 | 0.453 |
| 13 | " " | 3r | 0.218 | 0.667 |
| 14 | " " | 4r | 0.0922 | 0.855 |